PATENT SPECIFICATION

(11) 1 543 359

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(21) Application No. 44859/76 (22) Filed 28 Oct. 1976
(23) Complete Specification filed 26 Oct. 1977
(44) Complete Specification published 4 April 1979
(51) INT CL² C08F 8/14
(52) Index at acceptance
C3J CJ CS

(72) Inventors DIRK JAN VAN NAMEN and HENRICUS GEORGIUS PETER VAN DER VOORT

(54) ESTERIFICATION OF HYDROCARBYL-SUBSTITUTED SUCCINIC ANHYDRIDES

(71) We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V., a company organised under the laws of the Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention is concerned with a process for the preparation of esters of hydrocarbyl-substituted succinic anhydrides and with the esters so prepared.

Esters of hydrocarbyl-substituted succinic anhydrides are known products and are useful for many purposes e.g. as dispersant additives for lubricating oils (see U.K. 981,850; U.K. 1,055,337 and U.S. 3,576,743). A particularly useful ester is that prepared by reacting a hydrocarbyl-substituted succinic anhydride with pentaerythritol. The reaction product is usually a complex mixture of polyesters.

A general process for the preparation of these esters is given in U.K. 1,055,337. This general process comprises esterifying the hydrocarbyl-substituted succinic anhydride with pentaerythritol at elevated temperatures. Water vapour is produced during the reaction and this is removed from the reaction zone as the reaction proceeds. A solvent may be used in the process to facilitate the removal of water vapour from the reaction mixture. In addition the removal of water vapour may be facilitated by passing an inert gas e.g. nitrogen through the reaction mixture (see U.S. 3,576,743).

In all known processes for the esterification of hydrocarbyl-substituted succinic anhydride with pentaerythritol the water of esterification is removed from the reaction zone as the reaction proceeds. This is an obvious desideratum because the esterification reaction is an equilibrium reaction and the removal of the water is considered necessary in order to obtain a satisfactory conversion of the hydrocarbyl-substituted succinic anhydride.

One problem associated with the removal of the water is that some pentaerythritol is carried overhead with the vapours. Thus the ventilation of such vapours into the atmosphere is environmentally unacceptable. Alternatively the reactor vessel may be provided with a condenser for condensing the water vapour and, if a solvent is used, the solvent vapours. However, the cooling necessary to condense such vapours results in the sublimation of the pentaerythritol present therein on various parts of the reactor equipment e.g. on the top of the reaction vessel, overhead pipes and condenser. The pentaerythritol, which has a melting point of about 260°C, is deposited either as such or as a polycondensate thereof. This fouling of the reactor equipment is highly undesirable since it necessitates the periodic cleaning thereof.

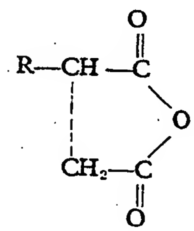
The Applicants have now surprisingly found that the reaction between hydrocarbyl-substituted succinic anhydrides and pentaerythritol may be carried out in a closed reaction vessel which substantially overcomes the disadvantage of the known processes.

This finding is considered surprising because it has been found that it is unnecessary to remove the water of esterification from the reaction zone during the course of the reaction in order to achieve satisfactory conversions of the hydrocarbyl-substituted succinic anhydrides. Consequently, condensation of the vapours is no longer necessary during the course of the reaction which means that the amount of pentaerythritol sublimation is substantially reduced. A further surprising finding is that the pressure build-up within the closed vessel is quite low, i.e. usually below 5 or 6 bars, which means that the reaction may be carried out in a glass or glass-lined closed reaction vessel; on theoretical grounds it would have been expected that the pressure build-up would be too high for such a vessel. A glass or glass-lined closed reaction vessel is desirable since the reactants and certain by-products are acidic.

Accordingly the invention is concerned with

a process for preparing esters of hydrocarbyl-substituted succinic anhydride and pentaerythritol which comprises reacting a hydrocarbyl-substituted succinic anhydride with pentaerythritol, characterized in that the reaction is carried out in closed reaction vessel.

The hydrocarbyl-substituted succinic anhydrides from which the esters are prepared are known products and may be represented by the general formula



wherein R is an alkyl or alkenyl group having from 30 to 700, suitably from 50 to 400, preferably from 50 to 200 carbon atoms. The hydrocarbyl substituent may contain non-hydrocarbyl groups, e.g. chloro or bromo groups, provided that such groups are not present in amounts sufficiently large to change the hydrocarbon nature of the substituent. The anhydrides may be prepared by known techniques such as by reacting a polymer of an olefin, e.g. C_2 to C_5 olefins, such as polybutylene, polyisobutylene or polypropylene, or a chloride thereof with maleic anhydride or by contacting a mixture of the polymer and maleic anhydride with chlorine. The preferred process comprises contacting the mixture of the polymer of the olefin and maleic anhydride with a molar deficiency of chlorine based on maleic anhydride. Those anhydrides prepared from chlorides or by using chlorine usually contain small amounts of residual chloro groups and are particularly corrosive since hydrogen chloride is formed during the reaction. Instead of the anhydride, the corresponding succinic acid may be charged to the reaction vessel. Such acids readily dehydrate at temperatures of above 100°C to produce the anhydrides which are then esterified with pentaerythritol.

The molar ratio of pentaerythritol to hydrocarbyl-substituted succinic anhydride used in the present invention may vary between wide limits. Suitably the molar ratio of pentaerythritol to hydrocarbyl-substituted succinic anhydride is from 0.25:1 to 4:1, preferably from 0.5:1 to 3.0:1. The pentaerythritol available commercially may contain up to 10% w of dipentaerythritol. The reaction temperature may also vary between wide limits with reaction temperatures from 140 to 255°C being suitable and from 170 to 230°C being preferred. The reaction time may also vary between wide limits with reaction times of from 2 to 48 hours being suitable. A solvent may also be present in the reaction mixture. Examples of solvents include hydrocarbons e.g. xylene, toluene and mineral oil; ethers e.g. diphenylether; ketones; and chlorobenzene. An esterification catalyst may also be added.

As stated hereinbefore the reaction is carried out in a closed reaction vessel. The term "closed reaction vessel" is well understood by those skilled in the art and means, insofar as the present invention is concerned, that substantially none of the vapour formed during the reaction, in particular the water vapour, is removed from the reaction zone during the course of the reaction. Thus such vapours are neither ventilated nor isolated by condensation during the course of the reaction. Consequently, substantially the only water present in the reaction zone is that which is dissolved in the reaction mixture and that which is present in the vapour phase. It is therefore not necessary to cool any part of the reaction vessel during the course of the reaction and in practice the reaction vessel may be thermally insulated which means that the internal temperature of the reaction vessel is substantially the same as that of the reaction mixture. Since no internal part of the reaction vessel communicates with the external atmosphere an autogeneous pressure build-up occurs. Suitably from 40 to 85% of the volume of the closed reaction vessel is filled with the reaction mixture. At the end of the reaction, which is when the desired conversion of anhydride has been achieved, the closed reaction vessel is opened and the water vapour, which contains no or substantiallly no pentaerythritol, is ventilated.

The reaction products obtained by the process according to the present invention may be worked-up by conventional techniques such as by the centrifugation or filtration and washing thereof.

The esters may be used in a variety of applications but are particularly suitable as oil additives e.g. fuels, including gasoline and middle distillate fuels, and crude oil. The esters are particularly suitable as lubricating oil, such as mineral lubricating oil, additives.

The invention will now be illustrated by reference to the following Examples. In the Examples the polyisobutylene-substituted succinic anhydride was obtained by passing chlorine through a mixture of polyisobutylene (MW 1,000) and maleic anhydride in the manner described in our co-pending Application No. 34599/75 (Serial No. 1,534,009).

EXAMPLE I
(Comparative)

A - litre open glass reaction vessel is charged with 500 g of a polyisobutylene-substituted succinic anhydride (acid number 1.63 meq KOH/g), 112 g of pentaerythritol (mole ratio of pentaerythritol to anhydride of 2:1)

and 37 g of xylene. This mixture was esterified at a temperature of 200°C with stirring for 24 hours. The water of esterification was continuously removed by means of the xylene acting as water transport agent. Water was separated from the xylene by means of Dean and Stark device. The reaction product was cooled to ambient temperature, diluted with an equal volume of gasoline and the unconverted pentaerythritol removed by centrifugation. The conversion of anhydride was found to be 96 % w, based on the amount of anhydride charged to the reaction vessel (acid number of product 0.06 meq KOH/g). During the reaction pentaerythritol sublimed on the top of the reaction vessel and the overhead system. The amount of sublimed material was determined and found to be 4 % w based on the amount of pentaerythritol charged to the reaction vessel.

EXAMPLE II

A 2 litre closed stainless steel autoclave was charged (about 60 % vol) with 815 g of polyisobutylene-substituted succinic anhydride (acid number 1.63 meq KOH/g) and 184 g of pentaerythritol (mole ratio of pentaerythritol to anhydride of 2:1). This mixture was esterified at a temperature of 200°C with stirring for 24 hours, after which the autoclave was opened, the reaction product cooled to ambient temperature, diluted with an equal volume of gasoline and the unconverted pentaerythritol removed by centrifugation. During the esterification reaction the pressure build up was about 4 bars. (The theoretical pressure build up is about 15 bars which is the vapour pressure of water at 200°C). The conversion of anhydride was found to be 90 % w (acid number of product 0.10 meq KOH/g).

The amount of sublimed material at the top of the reaction vessel was determined and found to be less than 0.1 % w based on the amount of pentaerythritol charged to the reaction vessel.

EXAMPLE III

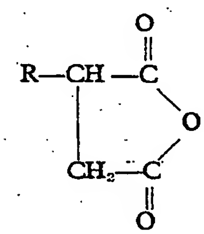
Example II was repeated using a glass-lined autoclave, a mole ratio of pentaerythritol to anhydride of 1.3:1 and a reaction time of 9 hours. Substantially the same results were obtained as for Example II except that no sublimed material was found in the reactor at the end of the reaction.

EXAMPLE IV

Example III was repeated using a mole ratio of pentaerythritol to anhydride of 1.3:1, a reaction temperature of 220°C and a reaction time of 12 hours. Substantially the same results were obtained as for Example II except that the pressure build-up was about 5 bars and that no sublimed material was found in the reactor at the end of the reaction.

WHAT WE CLAIM IS:—

1. A process for preparing esters of hydrocarbyl-substituted succinic anhydride and pentaerythritol comprising reacting a hydrocarbyl-substituted succinic anhydride with pentaerythritol, characterized in that the reaction is carried out in a closed reaction vessel.
2. A process as claimed in claim 1, characterized in that the anhydride has the general formula:



wherein R is an alkyl or alkenyl group having from 50 to 200 carbon atoms.
3. A process as claimed in claim 1 or claim 2, wherein the molar ratio of pentaerythritol to anhydride is from 0.25:1 to 4.0:1.
4. A process as claimed in any one of claims 1 to 3, wherein the reaction temperature is from 140 to 255°C.
5. A process as claimed in claim 1, substantially as hereinbefore described with particular reference to the Examples.
6. Esters of hydrocarbyl-substituted succinic anhydride whenever prepared by a process as claimed in any one of claims 1 to 5.

R. C. ROGERS,
Chartered Patent Agent,
Shell Centre,
London, S.E.1 7NA,
Agent for the Applicants.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1979
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.